Atomic decay near a quantized medium of absorbing scatterers

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Abstract. The decay of an excited atom in the presence of a medium that both scatters and absorbs radiation is studied with the help of a quantum-electrodynamical model. The medium is represented by a half space filled with a randomly distributed set of non-overlapping spheres, which consist of a linear absorptive dielectric material. The absorption effects are described by means of a quantized damped-polariton theory. It is found that the effective susceptibility of the bulk does not fully account for the medium-induced change in the atomic decay rate. In fact, surface effects contribute to the modification of the decay properties as well. The interplay of scattering and absorption in the total decay rate is discussed.

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1. Introduction

The spontaneous-emission rate of an excited atom can be altered by the atomic environment, as has been pointed out long ago [1]. For an atom embedded in a uniform linear non-absorptive dielectric of infinite extent the change in the emission rate has been obtained from quantum electrodynamics [2, 3]. For dense media local-field effects have to be considered as well [4, 5]. If the medium can absorb the emitted photons, the analysis gets more complicated, since the loss mechanism has to be treated in a quantum-mechanical context [6] - [14].

Local-field effects do not play a role if a different geometry is considered, with the atom situated outside a medium of finite (or semi-infinite) extent. A well-known case is that of an atom in front of a medium that fills a half-space. For this configuration the decay rate depends on the distance between the atom and the medium [15] - [22].

In all treatments mentioned so far the medium is structureless on the scale of the wavelength corresponding to the atomic transition. As a consequence, the medium properties are fully described by a susceptibility, which does not vary appreciably on the scale of the wavelength. The picture changes if the structure of the medium cannot be neglected, since scattering may occur then as well. The total extinction in such a medium is driven by both absorption and scattering. In practice, extinction by scattering in material media is quite common. Impurities and defects both lead to scattering effects that are difficult to avoid.

To study the interplay between the two types of extinction that may modify atomic decay processes in the presence of a material medium, it is useful to analyse a model in which both of these features occur simultaneously. The model that we shall adopt in the following is that of a medium consisting of non-overlapping spheres that are made of an absorptive material. The spheres, which may move freely through the system, are distributed randomly with a uniform average density. In a recent paper [23] a similar model with a collection of spherical scatterers consisting of non-absorptive material has been studied.

In order to describe the absorptive dielectric material of the spheres we shall use the quantum-mechanical damped-polariton model. The central quantity in this model is a space-dependent polarization density, which is coupled to the electromagnetic field and to a bath of harmonic oscillators accounting for absorption. The Hamiltonian of the damped-polariton model can be diagonalized exactly, as has been shown both for the case of a uniform dielectric [24] and for a dielectric with arbitrary inhomogeneities [25].

To arrive at analytical results for the decay rate in the presence of a medium with extinction due to both absorption and scattering we will adopt several approximations. The density of the spherical scatterers will supposed to be low, so that the medium is dilute. Furthermore, the size of the spheres will be taken to be small as compared to the atomic wavelength. Finally, the distance from the excited atom to the medium will be chosen to be large compared to the wavelength.

The paper is organized as follows. In section 2 the properties of the model and its diagonalization will be summarized. In section 3 the decay rate of an excited atom in the presence of an arbitrarily inhomogeneous damped-polariton dielectric will be derived from the basic Hamiltonian. The decay rate is determined by the electromagnetic Green function, which enters the description via a specific coefficient in the diagonalization matrix. Since the medium consists of randomly distributed spheres the Green function has to be averaged over all configurations in order to

obtain the physical decay rate. This averaging procedure will be discussed in section 4 and 5. As it turns out, the averaging process for a medium that fills a finite region of space (or a half-space) should be carried out carefully, since the boundaries give rise to specific surface contributions. Once these surface effects have been evaluated for the specific case of a medium filling a half-space, we can obtain the average decay rate of an excited atom in the presence of such a medium. The change in the atomic decay rate as a function of the distance between atom and medium will be determined in section 6, and the interplay of absorption and scattering processes will become clear. Some of the technical details of the derivation are given in two appendices.

2. Field quantization in the presence of an inhomogeneous absorbing dielectric medium

In the damped-polariton model the dielectric medium is described by a polarization density, which interacts with the electromagnetic field according to the standard minimal-coupling scheme. To account for absorption effects a bath of harmonic oscillators with a continuous range of eigenfrequencies is coupled to the polarization density in a bilinear way. The Hamiltonian of the model is [24, 25]

$$H_d = \int \mathrm{d}\mathbf{r} \left[\frac{1}{2\varepsilon_0}\Pi^2 + \frac{1}{2\mu_0}(\boldsymbol{\nabla}\times\mathbf{A})^2 + \frac{1}{2\rho}P^2 + \tfrac{1}{2}\rho\,\omega_0^2 X^2 + \frac{1}{2\rho}\int_0^\infty \mathrm{d}\omega\, Q_\omega^2 \right.$$
$$\left. + \tfrac{1}{2}\rho\int_0^\infty \mathrm{d}\omega\,\omega^2 Y_\omega^2 + \frac{\alpha}{\rho}\mathbf{A}\cdot\mathbf{P} + \frac{\alpha^2}{2\rho}A^2 + \frac{1}{\rho}\int_0^\infty \mathrm{d}\omega\, v_\omega\,\mathbf{X}\cdot\mathbf{Q}_\omega + \frac{1}{2\varepsilon_0}(\alpha\mathbf{X})_L^2 \right] . \tag{2.1}$$

The transverse part of the electromagnetic field is determined by the vector potential $\mathbf{A}(\mathbf{r})$, for which the Coulomb gauge is adopted. Its conjugate canonical momentum is $\boldsymbol{\Pi}(\mathbf{r})$. The linear dielectric, with a space-dependent density $\rho(\mathbf{r})$, is described by the harmonic displacement variable $\mathbf{X}(\mathbf{r})$ and its canonical momentum $\mathbf{P}(\mathbf{r})$, with the associated eigenfrequency $\omega_0(\mathbf{r})$. The electromagnetic field is coupled to the dielectric variables in the usual way. In terms of the polarization density $-\alpha(\mathbf{r})\mathbf{X}(\mathbf{r})$, with a space-dependent coupling parameter $\alpha(\mathbf{r}) > 0$, the minimal-coupling scheme leads to an electrostatic contribution involving $[\alpha(\mathbf{r})\mathbf{X}(\mathbf{r})]_L$ and to a bilinear interaction term with $\mathbf{A}(\mathbf{r})\cdot\mathbf{P}(\mathbf{r})$. The longitudinal part of a vector (or a tensor) is obtained by a convolution with the longitudinal delta function $\boldsymbol{\delta}_L(\mathbf{r}) = -\boldsymbol{\nabla}\boldsymbol{\nabla}(4\pi r)^{-1}$. Finally, damping is introduced in the system by a continuum bath of harmonic oscillators with canonical variables $\mathbf{Y}_\omega(\mathbf{r})$, $\mathbf{Q}_\omega(\mathbf{r})$ and with eigenfrequencies ω. These bath oscillators are coupled to $\mathbf{X}(\mathbf{r})$ with a strength $v_\omega(\mathbf{r}) > 0$.

The canonical variables obey the standard commutation relations:

$$[\boldsymbol{\Pi}(\mathbf{r}),\mathbf{A}(\mathbf{r}')] = -\mathrm{i}\hbar\,\boldsymbol{\delta}_T(\mathbf{r}-\mathbf{r}') \qquad [\mathbf{P}(\mathbf{r}),\mathbf{X}(\mathbf{r}')] = -\mathrm{i}\hbar\,\mathsf{I}\,\delta(\mathbf{r}-\mathbf{r}')$$
$$[\mathbf{Q}_\omega(\mathbf{r}),\mathbf{Y}_{\omega'}(\mathbf{r}')] = -\mathrm{i}\hbar\,\delta(\omega-\omega')\,\mathsf{I}\,\delta(\mathbf{r}-\mathbf{r}') \tag{2.2}$$

while all other commutators of the canonical variables vanish. Here I is the three-dimensional unit tensor, while $\boldsymbol{\delta}_T(\mathbf{r}) = \mathsf{I}\,\delta(\mathbf{r}) - \boldsymbol{\delta}_L(\mathbf{r})$ is the transverse delta function. The electric field operator $\mathbf{E}(\mathbf{r})$ is the sum of a transverse part depending on $\boldsymbol{\Pi}(\mathbf{r})$ and a longitudinal part that is proportional to the polarization density:

$$\mathbf{E}(\mathbf{r}) = -\frac{1}{\varepsilon_0}\boldsymbol{\Pi}(\mathbf{r}) + \frac{1}{\varepsilon_0}[\alpha(\mathbf{r})\mathbf{X}(\mathbf{r})]_L\,. \tag{2.3}$$

The Hamiltonian is quadratic in the canonical variables, and can be diagonalized explicitly [25]:

$$H_d = \int \mathrm{d}\mathbf{r} \int_0^\infty \mathrm{d}\omega \, \hbar\omega \, \mathbf{C}^\dagger(\mathbf{r},\omega) \cdot \mathbf{C}(\mathbf{r},\omega) \tag{2.4}$$

where we omit a zero-point-energy term. The operators $\mathbf{C}(\mathbf{r},\omega)$ are annihilation operators, which (together with the associated creation operators) satisfy the commutation relations:

$$\left[\mathbf{C}(\mathbf{r},\omega), \mathbf{C}^\dagger(\mathbf{r}',\omega')\right] = \delta(\omega-\omega') \, \mathsf{I} \, \delta(\mathbf{r}-\mathbf{r}') \qquad\qquad [\mathbf{C}(\mathbf{r},\omega), \mathbf{C}(\mathbf{r}',\omega')] = 0 \, . \tag{2.5}$$

Each canonical operator can be written as a linear combination of the annihilation and creation operators. For instance, one has

$$\mathbf{A}(\mathbf{r}) = \int \mathrm{d}\mathbf{r}' \int_0^\infty \mathrm{d}\omega \, \mathsf{f}_A(\mathbf{r},\mathbf{r}',\omega) \cdot \mathbf{C}(\mathbf{r}',\omega) + \mathrm{h.c.} \tag{2.6}$$

$$\mathbf{E}(\mathbf{r}) = \int \mathrm{d}\mathbf{r}' \int_0^\infty \mathrm{d}\omega \, \mathsf{f}_E(\mathbf{r},\mathbf{r}',\omega) \cdot \mathbf{C}(\mathbf{r}',\omega) + \mathrm{h.c.} \tag{2.7}$$

with the tensorial coefficients f_A and f_E. Similar expressions can be written for the other canonical variables. Since the vector potential is transverse, the coefficient f_A is transverse in $\mathbf{r}$.

In order to derive explicit expressions for the coefficients one may use a method due to Fano [26]. It amounts to evaluating the commmutator of $C(\mathbf{r},\omega)$ with the Hamiltonian H_d in two different ways. On the one hand this commutator follows from (2.4) and (2.5) as $[C(\mathbf{r},\omega), H_d] = \hbar\,\omega\, C(\mathbf{r},\omega)$, and on the other hand it may be evaluated by first writing $C(\mathbf{r},\omega)$ as a linear combination of the canonical variables, subsequently inserting (2.1) and finally employing (2.2). Upon solving the linear equations that follow by comparing the results of these two approaches, one arrives at explicit expressions for the coefficients in terms of the tensorial Green function G of the system [25]. The latter is defined as the solution of the standard equation

$$-\boldsymbol{\nabla} \times [\boldsymbol{\nabla} \times \mathsf{G}(\mathbf{r},\mathbf{r}',\omega+\mathrm{i}0)] + \frac{\omega^2}{c^2}\,[1+\chi(\mathbf{r},\omega+\mathrm{i}0)]\; \mathsf{G}(\mathbf{r},\mathbf{r}',\omega+\mathrm{i}0) = \mathsf{I}\,\delta(\mathbf{r}-\mathbf{r}') \tag{2.8}$$

with $\omega+\mathrm{i}0$ in the upper half of the complex plane and infinitesimally close to the positive real axis. In the course of the diagonalization process the frequency- and position-dependent susceptibility χ is found as

$$\chi(\mathbf{r},\omega{+}\mathrm{i}0) = -\frac{\alpha^2}{\varepsilon_0\rho}\left[\omega^2-\omega_0^2-\frac{1}{\rho^2}\int_0^\infty \mathrm{d}\omega' \,\frac{\omega'^2\, v_{\omega'}^2}{(\omega+\mathrm{i}0)^2-\omega'^2}\right]^{-1} . \tag{2.9}$$

The tensorial Green function satisfies the reciprocity relation

$$\tilde{\mathsf{G}}(\mathbf{r},\mathbf{r}',\omega+\mathrm{i}0) = \mathsf{G}(\mathbf{r}',\mathbf{r},\omega+\mathrm{i}0) \tag{2.10}$$

where the tilde denotes the tensor transpose. In terms of the above tensorial Green function, coefficients (2.6) and (2.7) are given as

$$\mathsf{f}_E(\mathbf{r},\mathbf{r}',\omega) = -i\,\frac{\omega^2}{c^2}\left(\frac{\hbar\,\mathrm{Im}\,\chi(\mathbf{r}',\omega+i0)}{\pi\varepsilon_0}\right)^{1/2} \mathsf{G}(\mathbf{r},\mathbf{r}',\omega+\mathrm{i}0) \tag{2.11}$$

$$\mathsf{f}_A(\mathbf{r},\mathbf{r}',\omega) = -\frac{i}{\omega}\,[\mathsf{f}_E(\mathbf{r},\mathbf{r}',\omega)]_T \, . \tag{2.12}$$

These expressions follow from the results presented in [25]. When they are substituted in (2.6) and (2.7), they lead to expressions for the vector potential and the electric field that agree with those postulated in a phenomenological quantization scheme [11], [13], [14].

3. Decay of an excited atom in the presence of an inhomogeneous absorbing dielectric

When a neutral atom at a fixed position is present as well, the total Hamiltonian H of the system is given by the sum $H_d + H_a + H_i$ of the damped-polariton Hamiltonian (2.1), the atomic Hamiltonian

$$H_a = \sum_i \frac{p_i^2}{2m} + \sum_{i \neq j} \frac{e^2}{8\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \frac{Ze^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_a|} \tag{3.1}$$

(with Z the atomic number, $\mathbf{r}_a$ the fixed position of the nucleus and $\mathbf{r}_i$, $\mathbf{p}_i$ the positions and momenta of the electrons) and the interaction Hamiltonian H_i, which follows from the usual minimal-coupling scheme as

$$H_i = \int \mathrm{d}\mathbf{r} [\rho_a(\mathbf{r})\, \varphi(\mathbf{r}) - \mathbf{J}_a(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})] \, . \tag{3.2}$$

Here $\rho_a(\mathbf{r}) = e \sum_i [\delta(\mathbf{r} - \mathbf{r}_a) - \delta(\mathbf{r} - \mathbf{r}_i)]$ and $\mathbf{J}_a(\mathbf{r}) = -\frac{1}{2} e \sum_i \{\mathbf{p}_i/m, \delta(\mathbf{r} - \mathbf{r}_i)\}$ are the local atomic charge and current densities, with curly brackets denoting the anticommutator. Furthermore, $\varphi(\mathbf{r})$ is the scalar potential due to the polarization of the dielectric. Its gradient is given by

$$\boldsymbol{\nabla}\varphi(\mathbf{r}) = -\frac{1}{\varepsilon_0} [\alpha(\mathbf{r})\, \mathbf{X}(\mathbf{r})]_L = -\mathbf{E}(\mathbf{r}) - \frac{1}{\varepsilon_0} \boldsymbol{\Pi}(\mathbf{r}) = -\mathbf{E}(\mathbf{r}) - \dot{\mathbf{A}}(\mathbf{r}) \tag{3.3}$$

with the time derivative given as $\dot{\mathbf{A}} = (\mathrm{i}/\hbar)[H, \mathbf{A}]$. In writing (3.2) we have assumed that local-field effects are negligible.

We assume that at the initial time $t = 0$, the atom is prepared in an excited state $|e\rangle$, while the dielectric medium (including the bath) and the electromagnetic field are in the ground state $|0\rangle$ of the Hamiltonian (2.1) or (2.4), i.e. in the state that is annihilated by all operators $\mathbf{C}(\mathbf{r}, \omega)$. The atom will decay to its ground state $|g\rangle$ with a time-dependent decay rate $\Gamma(t)$. This rate follows from perturbation theory in leading order as

$$\Gamma(t) = \frac{1}{\hbar^2} \sum_f \int_0^t \mathrm{d}t' \, \mathrm{e}^{(\mathrm{i}/\hbar)(E_f - E_i)t'} \, |\langle i|H_i|f\rangle|^2 + \mathrm{c.c.} \tag{3.4}$$

with $|i\rangle$ and $|f\rangle$ the initial and final states of the total system, with energies E_i and E_f, respectively.

Upon taking the matrix element of (3.2), using charge conservation in the form $\boldsymbol{\nabla} \cdot \mathbf{J}_a(\mathbf{r}) = -(\mathrm{i}/\hbar)[H_a, \rho_a(\mathbf{r})]$, carrying out a partial integration and substituting (3.3) with (2.6)-(2.7), we may rewrite the time-dependent decay rate as

$$\begin{aligned} \Gamma(t) = \frac{1}{\hbar^2 \omega_a^2} \int_0^t \mathrm{d}t' \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \int \mathrm{d}\mathbf{r}'' \int_0^\infty \mathrm{d}\omega \, \mathrm{e}^{\mathrm{i}(\omega - \omega_a)t'} \\ \langle e|\mathbf{J}_a(\mathbf{r}')|g\rangle \cdot [(\omega_a - \omega)\, \mathbf{f}_A(\mathbf{r}', \mathbf{r}, \omega) - \mathrm{i}\, \mathbf{f}_E(\mathbf{r}', \mathbf{r}, \omega)] \cdot \\ \cdot \left[(\omega_a - \omega)\, \tilde{\mathbf{f}}_A^*(\mathbf{r}'', \mathbf{r}, \omega) + \mathrm{i}\, \tilde{\mathbf{f}}_E^*(\mathbf{r}'', \mathbf{r}, \omega)\right] \cdot \langle g|\mathbf{J}_a(\mathbf{r}'')|e\rangle + \mathrm{c.c.} \end{aligned} \tag{3.5}$$

where $\hbar\omega_a$ is the difference between the energies of the excited and the ground state of the atom.

For large values of t the decay rate becomes independent of time. Carrying out the integrals over t' and ω one finds that the coefficient $\mathbf{f}_A$ drops out. As a result we get

$$\Gamma = \frac{2\pi}{\hbar^2 \omega_a^2} \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \int \mathrm{d}\mathbf{r}'' \, \langle e|\mathbf{J}_a(\mathbf{r}')|g\rangle \cdot \mathbf{f}_E(\mathbf{r}', \mathbf{r}, \omega_a) \cdot \tilde{\mathbf{f}}_E^*(\mathbf{r}'', \mathbf{r}, \omega_a) \cdot \langle g|\mathbf{J}_a(\mathbf{r}'')|e\rangle \, . \tag{3.6}$$

Inserting (2.11) we obtain

$$\Gamma = \frac{2\omega_a^2}{\varepsilon_0 \hbar c^4} \int d\mathbf{r}' \int d\mathbf{r}'' \, \langle e|\mathbf{J}_a(\mathbf{r}')|g\rangle \cdot \mathsf{F}(\mathbf{r}', \mathbf{r}'', \omega_a) \cdot \langle g|\mathbf{J}_a(\mathbf{r}'')|e\rangle \tag{3.7}$$

with the abbreviation

$$\mathsf{F}(\mathbf{r}', \mathbf{r}'', \omega) = \int d\mathbf{r} \, \mathsf{G}(\mathbf{r}', \mathbf{r}, \omega + i0) \cdot \tilde{\mathsf{G}}^*(\mathbf{r}'', \mathbf{r}, \omega + i0) \, \mathrm{Im}\, \chi(\mathbf{r}, \omega + i0)\,. \tag{3.8}$$

With the help of the differential equation (2.8) and the reciprocity relation (2.10) one may rewrite $\mathsf{F}(\mathbf{r}, \mathbf{r}', \omega)$ as $-(c/\omega)^2 \, \mathrm{Im}\, \mathsf{G}(\mathbf{r}, \mathbf{r}', \omega + i0)$, so that the decay rate gets the final form

$$\Gamma = -\frac{2}{\varepsilon_0 \hbar c^2} \int d\mathbf{r}' \int d\mathbf{r}'' \, \langle e|\mathbf{J}_a(\mathbf{r}')|g\rangle \cdot \mathrm{Im}\, \mathsf{G}(\mathbf{r}', \mathbf{r}'', \omega_a + i0) \cdot \langle g|\mathbf{J}_a(\mathbf{r}'')|e\rangle\,. \tag{3.9}$$

In the electric-dipole approximation the matrix element $\langle e|\mathbf{J}_a(\mathbf{r})|g\rangle$ is replaced by its localized form $\delta(\mathbf{r}-\mathbf{r}_a) \int d\mathbf{r} \langle e|\mathbf{J}_a(\mathbf{r})|g\rangle = i\, \delta(\mathbf{r}-\mathbf{r}_a)\, \omega_a \langle e|\boldsymbol{\mu}|g\rangle$, with $\boldsymbol{\mu} = -e \sum_i (\mathbf{r}_i - \mathbf{r}_a)$ the electric dipole moment. In that approximation the decay rate reads

$$\Gamma = -\frac{2\omega_a^2}{\varepsilon_0 \hbar c^2} \, \langle e|\boldsymbol{\mu}|g\rangle \cdot \mathrm{Im}\, \mathsf{G}(\mathbf{r}_a, \mathbf{r}_a, \omega_a + i0) \cdot \langle g|\boldsymbol{\mu}|e\rangle\,. \tag{3.10}$$

This expression for the decay rate, which is valid for an excited atom in the presence of an absorptive dielectric with arbitrary inhomogeneities, can be obtained as well by invoking the fluctuation-dissipation theorem [9, 13]. The above derivation shows how it follows from the explicit diagonalization of the inhomogeneous damped-polariton model in a rigorous way.

4. Medium of absorbing spherical scatterers

Let us consider a medium of non-overlapping spheres of absorptive material. It is an inhomogeneous dielectric that may be described by Hamiltonian (2.1). The susceptibility (2.9) has a constant value within the spheres and vanishes outside, so that it may be written as $\chi(\mathbf{r}, \omega + i0) = \chi(\omega + i0)\, f(\mathbf{r})$. If the radius of the spheres is a and the centre of the sphere i is located at $\mathbf{r}_i$ (with $|\mathbf{r}_i - \mathbf{r}_j| \geq 2a$ for $i \neq j$ so as to avoid overlap), the function $f(\mathbf{r})$ equals $\sum_i \theta(a - |\mathbf{r} - \mathbf{r}_i|)$, with the step function $\theta(x)$ equal to 1 for $x > 0$ and 0 elsewhere.

We are interested in the decay of an excited atom in the presence of such a medium of absorptive spheres. Since the spheres may move the effective decay rate follows from (3.9) or (3.10) by averaging over the positions of the centers of the spheres. Hence, we have to find an expression for the (imaginary part of the) average Green function.

The differential equation (2.8) for the Green function $\mathsf{G}(\mathbf{r}, \mathbf{r}', \omega + i0)$ is equivalent to an integral equation that relates G to the vacuum Green function G_0:

$$\mathsf{G}(\mathbf{r}, \mathbf{r}', z) = \mathsf{G}_0(\mathbf{r}, \mathbf{r}', z) - \frac{z^2}{c^2} \chi(z) \int d\mathbf{r}'' \, f(\mathbf{r}'')\, \mathsf{G}_0(\mathbf{r}, \mathbf{r}'', z) \cdot \mathsf{G}(\mathbf{r}'', \mathbf{r}', z) \tag{4.1}$$

with the frequency variable $z = \omega + i0$. The vacuum Green function is the solution of (2.8) with $\chi(\mathbf{r}, \omega + i0) = 0$. Iterating (4.1) we get a series of terms, which up to second order in the susceptibility reads

$$\begin{aligned} \mathsf{G}(\mathbf{r}, \mathbf{r}', z) &= \mathsf{G}_0(\mathbf{r}, \mathbf{r}', z) - \frac{z^2}{c^2} \chi(z) \int d\mathbf{r}'' \, f(\mathbf{r}'')\, \mathsf{G}_0(\mathbf{r}, \mathbf{r}'', z) \cdot \mathsf{G}_0(\mathbf{r}'', \mathbf{r}', z) \\ &+ \frac{z^4}{c^4} [\chi(z)]^2 \int d\mathbf{r}'' \int d\mathbf{r}''' \, f(\mathbf{r}'')\, f(\mathbf{r}''')\, \mathsf{G}_0(\mathbf{r}, \mathbf{r}'', z) \cdot \mathsf{G}_0(\mathbf{r}'', \mathbf{r}''', z) \cdot \mathsf{G}_0(\mathbf{r}''', \mathbf{r}', z) + \ldots \end{aligned} \tag{4.2}$$

When averaging both sides of this equation over the positions of the centers of the spheres, we need expressions for the averages $\langle f(\mathbf{r})\rangle$ and $\langle f(\mathbf{r})\, f(\mathbf{r}')\rangle$. When the centers of the spheres are uniformly distributed with the density n, these averages have the form

$$\langle f(\mathbf{r})\rangle = n\, v_0 \tag{4.3}$$

$$\begin{aligned}\langle f(\mathbf{r})\, f(\mathbf{r}')\rangle &= n \int \mathrm{d}\mathbf{r}''\, \theta(a-|\mathbf{r}-\mathbf{r}''|)\, \theta(a-|\mathbf{r}'-\mathbf{r}''|) \\ &+n^2 \int \mathrm{d}\mathbf{r}'' \int d\mathbf{r}'''\, \theta(a-|\mathbf{r}-\mathbf{r}''|)\, \theta(a-|\mathbf{r}'-\mathbf{r}'''|)\, g(\mathbf{r}'',\mathbf{r}''')\end{aligned} \tag{4.4}$$

with $v_0 = 4\pi a^3/3$ being the volume of the spheres and $g(\mathbf{r},\mathbf{r}')$ being the pair correlation function. If the spheres are dilutely distributed, the correlations may be neglected, so that g can be replaced by unity. Upon carrying out the geometrical integrals expression (4.4) becomes

$$\langle f(\mathbf{r})\, f(\mathbf{r}')\rangle = n\, \left[v_0 - \pi a^2\, |\mathbf{r}-\mathbf{r}'| + \tfrac{1}{12}\, \pi\, |\mathbf{r}-\mathbf{r}'|^3\right]\, \theta(2\, a - |\mathbf{r}-\mathbf{r}'|) + n^2\, v_0^2\, . \tag{4.5}$$

Inserting the above averages in the iterated integral equation (4.2), we get up to second order in the susceptibility:

$$\begin{aligned}\langle \mathbf{G}(\mathbf{r},\mathbf{r}',z)\rangle = \mathbf{G}_0(\mathbf{r},\mathbf{r}',z) - \frac{z^2}{c^2}\, n\, v_0\, \chi(z) \int d\mathbf{r}'' \int d\mathbf{r}'''\, \mathbf{G}_0(\mathbf{r},\mathbf{r}'',z)\, \cdot \\ \cdot \Bigg[\mathbf{I}\, \delta(\mathbf{r}''-\mathbf{r}''') - \frac{z^2}{c^2}\, \chi(z)\, n\, v_0\, \mathbf{G}_0(\mathbf{r}'',\mathbf{r}''',z) \\ -\frac{z^2}{c^2}\, \chi(z)\, c(|\mathbf{r}''-\mathbf{r}'''|)\, \mathbf{G}_0(\mathbf{r}'',\mathbf{r}''',z)\Bigg] \cdot \mathbf{G}_0(\mathbf{r}''',\mathbf{r}',z) + \ldots\end{aligned} \tag{4.6}$$

with the abbreviation

$$c(r) = \left(1 - \frac{3r}{4a} + \frac{r^3}{16a^3}\right)\, \theta(2\, a - r)\, . \tag{4.7}$$

The right-hand side is the iterated solution of the integral equation

$$\langle \mathbf{G}(\mathbf{r},\mathbf{r}',z)\rangle = \mathbf{G}_0(\mathbf{r},\mathbf{r}',z) - \frac{z^2}{c^2} \int d\mathbf{r}'' \int d\mathbf{r}'''\, \mathbf{G}_0(\mathbf{r},\mathbf{r}'',z) \cdot \boldsymbol{\chi}_e(\mathbf{r}'',\mathbf{r}''',z) \cdot \langle \mathbf{G}(\mathbf{r}''',\mathbf{r}',z)\rangle \tag{4.8}$$

again up to second order in $\chi(z)$. The effective susceptibility tensor is given as

$$\boldsymbol{\chi}_e(\mathbf{r},\mathbf{r}',z) = n\, v_0\, \chi(z)\, \left[\mathbf{I}\, \delta(\mathbf{r}-\mathbf{r}') - \frac{z^2}{c^2}\, \chi(z)\, c(|\mathbf{r}-\mathbf{r}'|)\, \mathbf{G}_0(\mathbf{r},\mathbf{r}',z)\right]\, . \tag{4.9}$$

It should be noted that the term proportional to $n^2\, [\chi(z)]^2$ in (4.6) results upon iterating (4.8) up to second order in $\boldsymbol{\chi}_e$.

The effective susceptibility (4.9) is non-local with a range equal to $2a$. The Green functions in the integrand of the last term of (4.8) do not change appreciably over that range, when a is small compared to c/ω (for $z = \omega + \mathrm{i}0$), and to $|\mathbf{r}-\mathbf{r}''|$ and $|\mathbf{r}'-\mathbf{r}'''|$. The first of these conditions can easily be met for spheres that are sufficiently small. In fact, we shall use (4.8) for ω equal to the atomic transition frequency, so that c/ω equals the transition wavelength. In contrast, the last two conditions are fulfilled only when $\mathbf{r}''$ and $\mathbf{r}'''$ in (4.8) are sufficiently far from the fixed positions $\mathbf{r}$ and $\mathbf{r}'$. Since the integrations in (4.8) extend over all parts of space accessible to the spheres, it is not obvious that the two conditions can be fulfilled. We will postpone a discussion of this point to the end of the section.

When all three conditions mentioned above are satisfied, one may replace $\boldsymbol{\chi}_e$ by its localized version. Quite generally the localized version of a function $F(\mathbf{r})$ that is of short range and centred around the origin can be written as a series expansion of which the first few terms are

$$F(\mathbf{r}) = \delta(\mathbf{r}) \int \mathrm{d}\mathbf{r}' \, F(\mathbf{r}') - [\boldsymbol{\nabla}\, \delta(\mathbf{r})] \cdot \int \mathrm{d}\mathbf{r}' \, \mathbf{r}' \, F(\mathbf{r}') + \tfrac{1}{2}[\boldsymbol{\nabla\nabla}\, \delta(\mathbf{r})] \, : \int \mathrm{d}\mathbf{r}' \, \mathbf{r}'\mathbf{r}' \, F(\mathbf{r}') + \ldots \tag{4.10}$$

We can evaluate the first few moments of $F(\mathbf{r}) = c(|\mathbf{r}|)\, \mathsf{G}_0(\mathbf{r}, 0, \omega + \mathrm{i}0)$ for small values of $q = \omega a/c$ by employing the expression [27, 28]

$$\begin{aligned}\mathsf{G}_0(\mathbf{r}, 0, z) = &-\frac{1}{4\pi r} \left(\mathsf{I} - \frac{\mathbf{rr}}{r^2}\right) \mathrm{e}^{\mathrm{i}zr/c} + \mathcal{P}\frac{1}{4\pi r} \left(-\mathrm{i}\, \frac{c}{zr} + \frac{c^2}{z^2r^2}\right) \left(\mathsf{I} - 3\frac{\mathbf{rr}}{r^2}\right) \mathrm{e}^{\mathrm{i}zr/c} \\ &+ \frac{c^2}{3z^2}\, \delta(\mathbf{r})\, \mathsf{I}\end{aligned} \tag{4.11}$$

for the vacuum Green function (with z in the upper part of the complex plane). The principal-value sign denotes the exclusion of an infinitely small spherical volume in subsequent integrations. As a result we obtain the following for the localized form of $\boldsymbol{\chi}_e$:

$$\begin{aligned}\boldsymbol{\chi}_e(\mathbf{r}, \mathbf{r}', z) = n\, v_0 \chi(z) &\left[1 - \chi(z) \left(\frac{1}{3} - \frac{4}{15}\, q^2 - \frac{2\mathrm{i}}{9}\, q^3\right)\right] \mathsf{I}\, \delta(\mathbf{r} - \mathbf{r}') \\ &- n\, v_0\, [\chi(z)]^2\, \frac{2}{75}\, a^2\, (\mathsf{I}\, \Delta - 3\boldsymbol{\nabla\nabla})\, \delta(\mathbf{r} - \mathbf{r}')\, .\end{aligned} \tag{4.12}$$

Here we have used the integral identities $\int d\Omega\, r_i\, r_j / r^2 = (4\pi/3)\, \delta_{ij}$ and $\int d\Omega\, r_i\, r_j\, r_k\, r_l / r^4 = (4\pi/15)\, (\delta_{ij}\, \delta_{kl} + \delta_{ik}\, \delta_{jl} + \delta_{il}\, \delta_{jk})$, with r_i being the cartesian components of the position vector $\mathbf{r}$ and $d\Omega$ being an element of solid angle in the direction of $\mathbf{r}$.

When the localized form (4.12) is inserted in (4.8) and a partial integration with respect to $\mathbf{r}''$ is carried out, we can employ the identity

$$(\mathsf{I}\, \Delta - 3\, \boldsymbol{\nabla\nabla}) \cdot \mathsf{G}_0(\mathbf{r}, \mathbf{r}', z) = -\frac{z^2}{c^2}\, \mathsf{G}_0(\mathbf{r}, \mathbf{r}', z) \tag{4.13}$$

for $\mathbf{r} \neq \mathbf{r}'$, as follows from the differential equation (2.8) (with $\chi = 0$) for the vacuum Green function. It should be noted that the second operator between the brackets in (4.13) does not contribute for $\mathbf{r} \neq \mathbf{r}'$, as is obvious from the form of the differential equation. There is no need to discuss the form that (4.13) may take for $\mathbf{r} = \mathbf{r}'$, since the localized form of the effective susceptibility can be used only when the arguments of the Green function are sufficiently far apart, as we have seen above.

When the identity (4.13) is taken into account, the localized form (4.12) of the effective susceptibility may be rewritten as

$$\boldsymbol{\chi}_e(\mathbf{r}, \mathbf{r}', z) = n\, v_0 \chi(z) \left[1 - \chi(z) \left(\frac{1}{3} - \frac{22}{75}\, q^2 - \frac{2\mathrm{i}}{9}\, q^3\right)\right] \mathsf{I}\, \delta(\mathbf{r} - \mathbf{r}') \equiv \chi_e(z)\, \mathsf{I}\, \delta(\mathbf{r} - \mathbf{r}')\, . \tag{4.14}$$

This localized form of the susceptibility has to be inserted in the integral equation (4.8). Its solution up to second order in $\chi(z)$ and up to first order in n reads

$$\langle \mathsf{G}(\mathbf{r}, \mathbf{r}', z) \rangle = \mathsf{G}_0(\mathbf{r}, \mathbf{r}', z) - \frac{z^2}{c^2}\, \chi_e(z) \int d\mathbf{r}''\, \mathsf{G}_0(\mathbf{r}, \mathbf{r}'', z) \cdot \mathsf{G}_0(\mathbf{r}'', \mathbf{r}', z). \tag{4.15}$$

In principle, this expression for the average Green function, with $\mathbf{r} = \mathbf{r}' = \mathbf{r}_a$ and $z = \omega_a + \mathrm{i}0$, could be used to evaluate the right-hand side of (3.10). When the medium of scattering and absorbing spheres is infinitely large, the atom is necessarily embedded in the medium. Since the integrals in (4.8) have to be taken over all space in that case, the integration variables $\mathbf{r}''$ and $\mathbf{r}'''$ can coincide with $\mathbf{r}_a$, so that the validity of the localized form (4.14) of the effective susceptibility is not guaranteed. This comes as no surprise, as local-field effects have to be taken into account in such a situation. We have to conclude that (4.15) cannot be used as such to determine the average decay rate of an excited atom in an infinite medium of absorptive spheres. However, one is often interested in a scattering medium of finite extent, in which the centers of the spheres are confined to a volume V (with $V/a^3 \gg 1$), while the excited atom is situated outside V. This configuration will be considered in the next section. The localized effective susceptibility is a useful concept in that case and the expression (4.15) for the average Green function can be employed, albeit after a suitable modification.

5. Finite media and surface effects

For a finite medium the expression for the average Green function has to be modified so as to include finite-volume effects. We start again from (4.2) and take the average over the positions of the centers of the spheres, which must be inside V. In lowest order of the susceptibility one encounters the average $\langle f(\mathbf{r})\rangle$, which for a uniformly distributed set of spheres with centers in V is given by

$$\langle f(\mathbf{r})\rangle = n\int^V d\mathbf{r}'\,\theta(a-|\mathbf{r}-\mathbf{r}'|) = n\,v_0\,\theta_V(\mathbf{r}) + n\left[\int^V d\mathbf{r}'\,\theta(a-|\mathbf{r}-\mathbf{r}'|) - v_0\,\theta_V(\mathbf{r})\right] \tag{5.1}$$

instead of (4.3). The step function $\theta_V(\mathbf{r})$ equals 1 for $\mathbf{r}$ inside V and vanishes elsewhere. The expression between square brackets differs from 0 only for positions $\mathbf{r}$ that are close to the surface of V, at a distance less than a. Assuming the surface to be approximately flat on that scale, one may write $\mathbf{r}$ as $\mathbf{r}_s + h\,\mathbf{n}$, with $\mathbf{r}_s$ a position vector at the surface and $\mathbf{n}$ a unit vector normal to the surface at $\mathbf{r}_s$ and pointing outwards. In that notation one finds

$$\langle f(\mathbf{r})\rangle = n\,v_0\,\theta_V(\mathbf{r}) + n\left[\tfrac{1}{2}\,v_0\,\varepsilon(h) - \pi\,a^2\,h + \tfrac{1}{3}\,\pi\,h^3\right]\,\theta(a-|h|) \tag{5.2}$$

with $\varepsilon(x) = \theta(x) - \theta(-x)$. As a consequence the contribution of $\langle\mathsf{G}\rangle$ that is linear in the susceptibility $\chi(z)$ gets the form

$$\begin{aligned}
&-\frac{z^2}{c^2}\,n\,v_0\,\chi(z)\int^V d\mathbf{r}''\,\mathsf{G}_0(\mathbf{r},\mathbf{r}'',z)\cdot\mathsf{G}_0(\mathbf{r}'',\mathbf{r}',z)\\
&-\frac{z^2}{c^2}\,n\,\chi(z)\int^S dS''\int_{-a}^{a} dh''\,\left[\tfrac{1}{2}\,v_0\,\varepsilon(h'') - \pi\,a^2\,h'' + \tfrac{1}{3}\,\pi\,h''^3\right]\\
&\times\mathsf{G}_0(\mathbf{r},\mathbf{r}''_s + h''\,\mathbf{n}'',z)\cdot\mathsf{G}_0(\mathbf{r}''_s + h''\,\mathbf{n}'',\mathbf{r}',z)\,.
\end{aligned} \tag{5.3}$$

The first term is the bulk contribution. It has the same form as the term linearly dependent on $\chi(z)$ in (4.15), with the integration extended over V only. The second term is the surface contribution. Here dS'' is a surface element at $\mathbf{r}''_s$, with a local normal unit vector $\mathbf{n}''$.

The surface contribution in (5.3) may be evaluated as follows. Let us assume that both $\mathbf{r}$ and $\mathbf{r}'$ are far outside the volume, so that both $|\mathbf{r}-\mathbf{r}''_s|$ and $|\mathbf{r}'-\mathbf{r}''_s|$ are much larger than the wavelength (which itself is much larger than the radius of the spheres). In that case the dependence of the Green functions G_0 on h'' is determined by a phase factor, as follows from (4.11). As a consequence one may write

$$\mathsf{G}_0(\mathbf{r},\mathbf{r}''_s+h''\,\mathbf{n}'',z)\cdot\mathsf{G}_0(\mathbf{r}''_s+h''\,\mathbf{n}'',\mathbf{r}',z)= \\ =\mathsf{G}_0(\mathbf{r},\mathbf{r}''_s,z)\cdot\mathsf{G}_0(\mathbf{r}''_s,\mathbf{r}',z)\,\mathrm{e}^{-\mathrm{i}\,z\,h''\,\mathbf{n}''\cdot(\mathbf{e}_s+\mathbf{e}'_s)/c} \tag{5.4}$$

with $\mathbf{e}_s$ and $\mathbf{e}'_s$ being unit vectors in the direction $\mathbf{r}-\mathbf{r}''_s$ and $\mathbf{r}'-\mathbf{r}''_s$, respectively. For $z=\omega+\mathrm{i}\,0$ and $q=\omega a/c\ll 1$, as before, the exponential can be expanded. Subsequently, upon evaluating the integral over h'' in (5.3) we arrive at a surface contribution of the form

$$\mathrm{i}\,\frac{z^2}{10c^2}\,n\,v_0\,\chi(z)\,a\,q\int^S dS''\,\mathbf{n}''\cdot(\mathbf{e}_s+\mathbf{e}'_s)\,\mathsf{G}_0(\mathbf{r},\mathbf{r}''_s,z)\cdot\mathsf{G}_0(\mathbf{r}''_s,\mathbf{r}',z)\,. \tag{5.5}$$

With the use of Gauss's theorem, the surface integral can be transformed to a volume integral. Since $\mathbf{r}$ and $\mathbf{r}'$ are both far from the surface, the ensuing differentiation operator can be taken to act on the phase factors in the Green functions only. Carrying out these differentiations we finally arrive at the following expression for the surface contribution in $\langle\mathsf{G}\rangle$ that is linear in the susceptibility:

$$\frac{z^2}{5c^2}\,n\,v_0\,\chi(z)\,q^2\int^V d\mathbf{r}''\,(1+\mathbf{e}\cdot\mathbf{e}')\,\mathsf{G}_0(\mathbf{r},\mathbf{r}'',z)\cdot\mathsf{G}_0(\mathbf{r}'',\mathbf{r}',z) \tag{5.6}$$

with $\mathbf{e}$ being a unit vector in the direction of $\mathbf{r}-\mathbf{r}''$ and an analogous unit vector $\mathbf{e}'$. The integrand vanishes for all points $\mathbf{r}''$ that lie on the line connecting $\mathbf{r}$ and $\mathbf{r}'$, i.e. for forward scattering at the spheres, since $\mathbf{e}=-\mathbf{e}'$ in that case. For backward scattering the correction does not vanish.

In second order of the susceptibility one needs an expression for $\langle f(\mathbf{r})\,f(\mathbf{r}')\rangle$ which takes account of finite-volume effects. Analogously to (5.1) we write

$$\begin{aligned}\langle f(\mathbf{r})\,f(\mathbf{r}')\rangle-\langle f(\mathbf{r})\rangle\,\langle f(\mathbf{r}')\rangle=n\int^V d\mathbf{r}''\,\theta(a-|\mathbf{r}-\mathbf{r}''|)\,\theta(a-|\mathbf{r}'-\mathbf{r}''|)= \\ =n\,\theta_V(\mathbf{r})\int d\mathbf{r}''\,\theta(a-|\mathbf{r}-\mathbf{r}''|)\,\theta(a-|\mathbf{r}'-\mathbf{r}''|) \\ +n\left[\int^V d\mathbf{r}''\,\theta(a-|\mathbf{r}-\mathbf{r}''|)\,\theta(a-|\mathbf{r}'-\mathbf{r}''|)\right. \\ \left.-\,\theta_V(\mathbf{r})\int d\mathbf{r}''\,\theta(a-|\mathbf{r}-\mathbf{r}''|)\,\theta(a-|\mathbf{r}'-\mathbf{r}''|)\right]\end{aligned} \tag{5.7}$$

where correlation effects have been omitted, as before. The first term at the right-hand side leads to a volume contribution. After proper localization one finds an expression of the same form as the term of order $[\chi(z)]^2$ in (4.15) with (4.14), with the integration extended over V.

The remaining terms at the right-hand side of (5.7) vanish when $\mathbf{r}$ and/or $\mathbf{r}'$ are far from the surface. In fact, one may rewrite $\theta_V(\mathbf{r}'')-\theta_V(\mathbf{r})$ as $[1-\theta_V(\mathbf{r})]\theta_V(\mathbf{r}'')-\theta_V(\mathbf{r})\,[1-\theta_V(\mathbf{r}'')]$, so that $\mathbf{r}$ and $\mathbf{r}''$ must be on different sides of the surface. Since the θ-functions in (5.7) imply that these positions can at most be a distance a apart, they are within a distance a from the surface. As a consequence, the contribution of the

second term in (5.7) to the average Green function is a surface term. After a suitable change of variables it can be written as

$$\frac{z^4}{c^4}\, n\, [\chi(z)]^2 \int^S dS'' \int dh'' \int^S dS''' \int dh'''\, \mathsf{G}_0(\mathbf{r}, \mathbf{r}''_s + h''\, \mathbf{n}'', z) \cdot$$
$$\cdot \mathsf{G}_0(\mathbf{r}''_s + h''\, \mathbf{n}'', \mathbf{r}'''_s + h'''\, \mathbf{n}''', z) \cdot \mathsf{G}_0(\mathbf{r}'''_s + h'''\, \mathbf{n}''', \mathbf{r}', z)\, F(\mathbf{r}''_s, \mathbf{r}'''_s, h'', h''')\,. \qquad (5.8)$$

The function F is defined as

$$F(\mathbf{r}_s, \mathbf{r}'_s, h, h') = \int dS'' \int dh'' \, \left[-\theta(-h)\, \theta(h'' + \tfrac{1}{2}(h+h')) + \theta(h)\, \theta(-h'' - \tfrac{1}{2}(h+h'))\right]$$
$$\times \theta\left(a - |\mathbf{r}_s + \tfrac{1}{2}(h-h')\, \mathbf{n} - \mathbf{r}''_s - h''\, \mathbf{n}|\right) \theta\left(a - |\mathbf{r}'_s - \tfrac{1}{2}(h-h')\, \mathbf{n} - \mathbf{r}''_s - h''\, \mathbf{n}|\right)\,. \qquad (5.9)$$

The normal unit vectors at $\mathbf{r}_s$, $\mathbf{r}'_s$ and $\mathbf{r}''_s$ can be taken identical since these positions are at most a distance $2a$ apart. For the same reason the second Green function in (5.8) can be replaced by its short-range approximation:

$$\mathsf{G}_0(\mathbf{r}, 0, z) \simeq \frac{c^2}{z^2}\, \mathcal{P} \frac{1}{4\pi r^3} \left(\mathsf{I} - 3\frac{\mathbf{r}\mathbf{r}}{r^2}\right) + \frac{c^2}{3z^2}\, \delta(\mathbf{r})\, \mathsf{I} \qquad (5.10)$$

as follows from (4.11). After substitution of this expression and of (5.9) in (5.8) the contribution of the delta function in (5.10) can be evaluated along the same lines as before. One finds the following on a par with (5.5):

$$-\, \mathrm{i}\, \frac{z^2}{30c^2}\, n\, v_0\, [\chi(z)]^2\, a\, q \int^S dS''\, \mathbf{n}'' \cdot (\mathbf{e}_s + \mathbf{e}'_s)\, \mathsf{G}_0(\mathbf{r}, \mathbf{r}''_s, z) \cdot \mathsf{G}_0(\mathbf{r}''_s, \mathbf{r}', z)\,. \qquad (5.11)$$

The evaluation of the contribution from the dyadic part of (5.10) is more complicated. Some of the details are given in appendix A. The result is

$$-\, \mathrm{i}\, \frac{z^2}{25c^2}\, n\, v_0\, [\chi(z)]^2\, a\, q \int^S dS''\, \mathsf{G}_0(\mathbf{r}, \mathbf{r}''_s, z) \cdot (-\tfrac{2}{3}\, \mathsf{I}\, \mathbf{n}'' \cdot \mathbf{e}'_s + \mathbf{e}'_s\, \mathbf{n}'') \cdot \mathsf{G}_0(\mathbf{r}''_s, \mathbf{r}', z)\,. \qquad (5.12)$$

A further term of second order in $\chi(z)$ arises from the uncorrelated part $\langle f(\mathbf{r})\rangle \langle f(\mathbf{r}')\rangle$ of $\langle f(\mathbf{r})\, f(\mathbf{r}')\rangle$, as given in (5.7). Since it is proportional to n^2 it is negligible for a dilute set of scatterers.

The complete set of terms that result from surface effects in second order of the susceptibility $\chi(z)$ is found by adding (5.11) and (5.12):

$$-\, \mathrm{i}\, \frac{z^2}{25c^2}\, n\, v_0\, [\chi(z)]^2\, a\, q \int^S dS''\, \mathsf{G}_0(\mathbf{r}, \mathbf{r}''_s, z) \cdot \left[\tfrac{1}{6} \mathsf{I}\, \mathbf{n}'' \cdot (5\mathbf{e}_s + \mathbf{e}'_s) + \mathbf{e}'_s\, \mathbf{n}''\right] \cdot$$
$$\cdot \mathsf{G}_0(\mathbf{r}''_s, \mathbf{r}', z)\,. \qquad (5.13)$$

As before we may use Gauss's theorem to write this expression as a volume integral:

$$-\, \frac{z^2}{25c^2}\, n\, v_0\, [\chi(z)]^2\, q^2 \int^V d\mathbf{r}''\, \mathsf{G}_0(\mathbf{r}, \mathbf{r}'', z) \cdot [\mathsf{I}\, (1 + \mathbf{e} \cdot \mathbf{e}') + \mathbf{e}'\, \mathbf{e}] \cdot \mathsf{G}_0(\mathbf{r}'', \mathbf{r}', z)\,. \qquad (5.14)$$

As in (5.6) the integrand vanishes for forward scattering, since $\mathbf{e} = -\mathbf{e}'$ in that case and $\mathsf{G}_0(\mathbf{r}, \mathbf{r}'', z) \cdot \mathbf{e} = 0$ for large $|\mathbf{r} - \mathbf{r}''|$.

In conclusion, we have found an expression for the average Green function $\langle \mathsf{G}(\mathbf{r}, \mathbf{r}', z)\rangle$ of a dilute set of spherical scatterers inside a volume V. The expression is valid up to first order in the density and second order in the susceptibility and for positions $\mathbf{r}$ and $\mathbf{r}'$ far outside V. Its bulk part is given by (4.15) (with volume

integrations extended over V), while the contribution from the surface is the sum of (5.5) (or (5.6)) and (5.13) (or (5.14)). The complete result is

$$\begin{aligned}
&\langle \mathsf{G}(\mathbf{r},\mathbf{r}',z)\rangle = \mathsf{G}_0(\mathbf{r},\mathbf{r}',z)\\
&-\frac{z^2}{c^2}\, n\, v_0\, \chi(z) \int^V d\mathbf{r}''\ \left[1-\tfrac{1}{5}\, q^2\, (1+\mathbf{e}\cdot\mathbf{e}')\right] \mathsf{G}_0(\mathbf{r},\mathbf{r}'',z)\cdot \mathsf{G}_0(\mathbf{r}'',\mathbf{r}',z)\\
&+\frac{z^2}{c^2}\, n\, v_0\, [\chi(z)]^2 \int^V d\mathbf{r}''\, \mathsf{G}_0(\mathbf{r},\mathbf{r}'',z)\cdot \left[\mathsf{I}\left(\frac{1}{3}-\frac{1}{3}\,q^2-\frac{1}{25}\,q^2\,\mathbf{e}\cdot\mathbf{e}'-\frac{2\mathrm{i}}{9}\,q^3\right)-\frac{1}{25}\,q^2\,\mathbf{e}'\,\mathbf{e}\right]\\
&\qquad\qquad \cdot \mathsf{G}_0(\mathbf{r}'',\mathbf{r}',z)\,. \qquad (5.15)
\end{aligned}$$

To check this expression we use it to derive the electric field generated by a source far away from the volume V. The Fourier component $\mathbf{E}(\mathbf{r},\omega)$ of the electric field follows from the current density component $\mathbf{J}(\mathbf{r},\omega)$ of the source as

$$\mathbf{E}(\mathbf{r},\omega) = -\mathrm{i}\,\mu_0\,\omega \int d\mathbf{r}'\,\mathsf{G}(\mathbf{r},\mathbf{r}',\omega+\mathrm{i}0)\cdot \mathbf{J}(\mathbf{r}',\omega)\,. \qquad (5.16)$$

If the source is such that in the absence of the medium the electric field is a plane wave with Fourier component $\mathbf{E}_i(\mathbf{r},\omega) = E_0\,\mathbf{e}_\sigma\,\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r})$, with $\mathbf{e}_\sigma$ being a polarization vector, the average of the full electric-field component $\mathbf{E}(\mathbf{r},\omega)$, including the response of the medium, is obtained from (5.15) as

$$\begin{aligned}
&\langle \mathbf{E}(\mathbf{r},\omega)\rangle = \mathbf{E}_i(\mathbf{r},\omega)\\
&-\frac{\omega^2}{c^2}\, n\, v_0\, \chi(\omega+\mathrm{i}0) \int^V d\mathbf{r}''\ \left[1-\tfrac{1}{5}\, q^2\, (1-\mathbf{e}\cdot\hat{\mathbf{k}})\right] \mathsf{G}_0(\mathbf{r},\mathbf{r}'',\omega+\mathrm{i}0)\cdot \mathbf{E}_i(\mathbf{r}'',\omega)\\
&+\frac{\omega^2}{c^2}\, n\, v_0\, [\chi(\omega+\mathrm{i}0)]^2 \int^V d\mathbf{r}''\, \mathsf{G}_0(\mathbf{r},\mathbf{r}'',\omega+\mathrm{i}0)\,\cdot\\
&\qquad \cdot\left[\mathsf{I}\left(\frac{1}{3}-\frac{1}{3}\,q^2+\frac{1}{25}\,q^2\,\mathbf{e}\cdot\hat{\mathbf{k}}-\frac{2\mathrm{i}}{9}\,q^3\right)+\frac{1}{25}\,q^2\,\hat{\mathbf{k}}\,\mathbf{e}\right]\cdot \mathbf{E}_i(\mathbf{r}'',\omega)\,. \qquad (5.17)
\end{aligned}$$

As before, $\mathbf{e}$ is a unit vector in the direction $\mathbf{r}-\mathbf{r}''$. The unit vector $\mathbf{e}'$ in (5.15) could be replaced by minus the unit vector $\hat{\mathbf{k}}$ in the direction of the wave vector of the incoming wave. The expression found here is consistent with that obtained for the average scattered field from a collection of dielectric spheres in Mie theory, as is shown in appendix B.

The above derivation of the average Green function in the presence of a finite volume filled with absorbing scatterers clearly shows how in general both bulk and surface effects contribute in producing the complete result. A naive treatment in which the surface effects are neglected does not yield the correct answer, when the spheres are of a finite extent. The surface contributions account for the coarseness of the surface, which arises from the fact that some of the spheres may protrude. These protrusions give rise to specific terms in the average Green function that do not occur for an infinite medium.

6. Atomic decay near a half-space of absorptive scatterers

We consider an excited atom in the presence of a medium of absorptive scatterers that fills the complete half-space $z<0$. The atomic position is $(0,0,z_a)$, with $z_a>0$. We assume $z_a\,\omega_a/c \gg 1$, so that the results of the previous sections can be applied. In

the electric-dipole approximation the average decay rate follows from (3.10) by taking the average over the position of the scatterers:

$$\langle\Gamma\rangle = -\frac{2\omega_a^2}{\varepsilon_0\hbar c^2}\,\langle e|\boldsymbol{\mu}|g\rangle\cdot\mathrm{Im}\,\langle\mathbf{G}(\mathbf{r}_a,\mathbf{r}_a,\omega_a+\mathrm{i}0)\rangle\cdot\langle g|\boldsymbol{\mu}|e\rangle\,. \tag{6.1}$$

At the right-hand side we substitute expression (5.15) for the average Green function. The leading term yields the standard vacuum decay rate

$$\Gamma_0 = \frac{\omega_a^3}{3\pi\varepsilon_0\hbar c^3}\,|\langle e|\boldsymbol{\mu}|g\rangle|^2\,. \tag{6.2}$$

The next term in (5.15) leads to a first correction in $\langle\mathbf{G}(\mathbf{r}_a,\mathbf{r}_a,\omega_a+\mathrm{i}0)\rangle$ of the form

$$-\frac{\omega_a^2}{c^2}\,n\,v_0\,\chi(\omega_a+\mathrm{i}0)\,(1-\tfrac{2}{5}\,q^2)\int^V d\mathbf{r}\,\mathbf{G}_0(\mathbf{r}_a,\mathbf{r},\omega_a+\mathrm{i}0)\cdot\mathbf{G}_0(\mathbf{r},\mathbf{r}_a,\omega_a+\mathrm{i}0) \tag{6.3}$$

since $\mathbf{e}=\mathbf{e}'$ in the present case. The integral is a diagonal tensor, with equal xx- and yy-components, and a zz-component that is different. For the xx- and yy-components we find the following upon substituting the long-range form of the vacuum Green function (4.11) and using cylinder coordinates:

$$\int_{z_a}^{\infty}dz\int_0^{\infty}d\rho\,\rho\,\frac{2z^2+\rho^2}{16\pi(z^2+\rho^2)^2}\,\exp\left[2\mathrm{i}\,\frac{\omega_a+\mathrm{i}0}{c}\,(z^2+\rho^2)^{1/2}\right]. \tag{6.4}$$

Introducing the new variable $t=[z^2+\rho^2]^{1/2}/z_a$ instead of ρ and carrying out the integrals, we get

$$\frac{z_a}{16\pi}\,\left[\tfrac{4}{3}\,E_0(u)-E_1(u)-\tfrac{1}{3}\,E_3(u)\right] \tag{6.5}$$

with $u=-2\mathrm{i}\,z_a\,(\omega_a+\mathrm{i}0)/c$ and with the functions

$$E_n(x)=\int_1^{\infty}dt\,\frac{\mathrm{e}^{-xt}}{t^n} \tag{6.6}$$

for a non-negative integer n and for x in the right half of the complex plane. Since for large $|x|$ these functions are given by their asymptotic expansions

$$E_n(x)=\frac{\mathrm{e}^{-x}}{x}\,\left[1-\frac{n}{x}+\frac{n(n+1)}{x^2}+\ldots\right] \tag{6.7}$$

the xx- and yy-components of the second term in (5.15) read

$$\frac{1}{32\pi}\,n\,v_0\,\chi(\omega_a+\mathrm{i}0)\,\left(1-\frac{2}{5}\,q^2\right)\frac{\mathrm{e}^{2\mathrm{i}z_a\omega_a/c}}{z_a}\,. \tag{6.8}$$

A similar calculation leads to the conclusion that the corresponding zz-component is inversely proportional to z_a^2 so that it is small for large values of $z_a\,\omega_a/c$.

The last term of (5.15) can be evaluated in an analogous way. Upon using the identity $\mathbf{G}_0(\mathbf{r},\mathbf{r}'',\omega_a+\mathrm{i}0)\cdot\mathbf{e}=0$ for large $|\mathbf{r}-\mathbf{r}''|\,\omega_a/c$, the xx- and yy-components are found as

$$-\frac{1}{32\pi}\,n\,v_0\,[\chi(\omega_a+\mathrm{i}0)]^2\,\left(\frac{1}{3}-\frac{28}{75}\,q^2-\frac{2\mathrm{i}}{9}\,q^3\right)\frac{\mathrm{e}^{2\mathrm{i}z_a\omega_a/c}}{z_a} \tag{6.9}$$

while the zz-component is inversely proportional to z_a^2, as before.

Collecting all results, we have found the following expression for the average decay rate of an excited atom in the presence of a semi-infinite medium of absorbing spherical scatterers:

$$\langle\Gamma\rangle = \Gamma_0 - \frac{3}{16}\, n\, v_0\, \Gamma_{0,\perp}$$
$$\times \mathrm{Im}\left\{\left[1 - \frac{2}{5}\, q^2 - \left(\frac{1}{3} - \frac{28}{75}\, q^2 - \frac{2\mathrm{i}}{9}\, q^3\right)\, \chi(\omega_a + \mathrm{i}0)\right]\, \chi(\omega_a + \mathrm{i}0)\, \frac{\mathrm{e}^{2\mathrm{i}\zeta_a}}{\zeta_a}\right\} \tag{6.10}$$

for large values of the dimensionless distance $\zeta_a = z_a\omega_a/c$ between the atom and the medium. Here $\Gamma_{0,\perp}$ is given by (6.2), with $\boldsymbol{\mu}$ replaced by the projection $\boldsymbol{\mu}_\perp$ of $\boldsymbol{\mu}$ on the plane parallel to the interface of the medium.

In deriving the above result we have taken due account of the surface effects. The terms of order q^2 would have been determined incorrectly, if the contributions of section 5 had been missed. As we have seen, the latter contributions correct for the fact that protruding spheres cause surface coarseness.

Expression (6.10) is the main result of this paper. It shows the interplay of absorption and scattering effects in the modification of the average decay rate. For spheres that do not absorb at the atomic frequency, so that $\chi(\omega_a)$ is real, the average decay rate can be rewritten as

$$\langle\Gamma\rangle = \Gamma_0 - \frac{3}{16}\, n\, v_0\, \Gamma_{0,\perp}\, \left\{\left[1 - \frac{2}{5}\, q^2 - \left(\frac{1}{3} - \frac{28}{75}\, q^2\right)\, \chi(\omega_a)\right]\, \chi(\omega_a)\, \frac{\sin(2\zeta_a)}{\zeta_a}\right.$$
$$\left. + \frac{2}{9}\, q^3\, [\chi(\omega_a)]^2\, \frac{\cos(2\zeta_a)}{\zeta_a}\right\}\, . \tag{6.11}$$

On the other hand, if absorption plays a role, whereas scattering effects can be neglected (as is the case for spheres with $q \approx 0$), one has

$$\langle\Gamma\rangle = \Gamma_0 - \frac{3}{16}\, n\, v_0\, \Gamma_{0,\perp}\, \left[\left\{\chi_r(\omega_a) - \frac{1}{3}[\chi_r(\omega_a)]^2 + \frac{1}{3}[\chi_i(\omega_a)]^2\right\}\, \frac{\sin(2\zeta_a)}{\zeta_a}\right.$$
$$\left. + \left\{1 - \frac{2}{3}\chi_r(\omega_a)\right\}\, \chi_i(\omega_a)\, \frac{\cos(2\zeta_a)}{\zeta_a}\right] \tag{6.12}$$

with $\chi_r(\omega)$ and $\chi_i(\omega)$ being the real and imaginary part of $\chi(\omega+\mathrm{i}0)$, respectively. The decay rate for an excited atom in front of an absorbing dielectric half-space without scattering has been determined before, as we noted in section 2. From the results in [17, 19] one derives (after a few minor amendments) a decay rate for large ζ_a that coincides with (6.12), when the effective susceptibility (4.14) for $q \to 0$ is introduced.

In figure 1 the decay rate correction function, defined as $f(\zeta_a) = -16\,(\langle\Gamma\rangle - \Gamma_0)/(3\, n\, v_0\, \Gamma_{0,\perp})$, is given as a function of ζ_a for two specific choices of the parameters q and $\chi(\omega_a)$, corresponding to a purely scattering case, with a decay rate given by (6.11), and to a purely absorbing case, with decay rate (6.12). Both curves show a characteristic interference pattern. Depending on the precise location of the atom, the decay rate is either enhanced or reduced with respect to the vacuum decay rate. The effect is larger for absorbing spheres than for scattering spheres. Moreover, the phase of the damped oscillations of the two curves is different. For absorbing spheres the positions of the extrema are somewhat nearer to the interface than for scattering spheres.

Interference fringes in emission processes due to reflection at an ideal mirror have been observed experimentally [29]. The modification of radiative properties near a dielectric medium has been determined experimentally a few years ago as well [22].

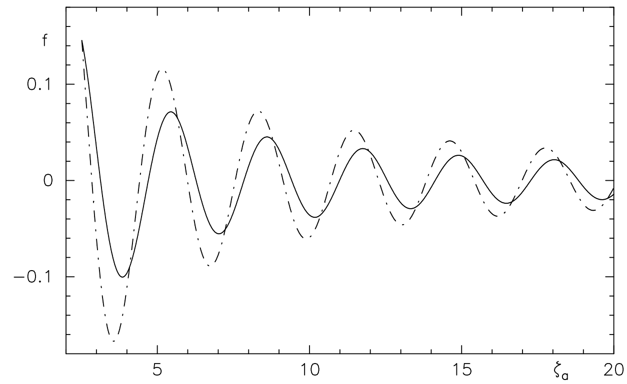

Figure 1. Decay rate correction function $f(\zeta_a) = -16\,(\langle\Gamma\rangle - \Gamma_0)/(3\,n\,v_0\,\Gamma_{0,\perp})$ for a medium with scattering spheres (with $q = 0.5$, $\chi(\omega_a) = 0.5$, ——) and for a medium with absorbing spheres (with $q = 0$, $\chi(\omega_a) = 0.5 + \mathrm{i}\,0.5$, — · —).

It would be interesting to measure the influence of absorption and scattering in the medium on the emission processes and to compare the results with those found here.

7. Conclusion and outlook

In this paper we have shown how both scattering and absorption effects can play a role in the decay of an excited atom in the vicinity of a dielectric medium. Since atomic decay is essentially a non-classical phenomenon, a consistent treatment requires the use of a quantum-mechanical description for the scattering and absorbing dielectric medium, for the atom and for the electromagnetic fields through which they interact. As we have seen, a convenient model that suits these requirements is furnished by an inhomogeneous damped-polariton model for a set of absorptive dielectric spheres that scatter incoming light. In contrast to what one might expect, the average bulk properties of such a granular medium are in general not sufficient to account for all effects of scattering on the atomic decay, at least for spheres with a finite size as compared to the atomic wavelength. In fact, under these circumstances the effective dielectric constant for the bulk does not yield all information on the scattering processes. A subtle surface effect in the scattering contributes to the change of the decay as well. Only when this surface contribution is taken into account does one obtain the complete expression for the modified decay rate.

In our treatment we have confined ourselves to a description of a dilute medium in which multiple-scattering effects are negligible. Moreover, we have considered only the first few terms in an expansion of the scattering amplitudes with respect to the ratio of the spherical diameter and the atomic wavelength. It would be interesting to see whether the above findings about the importance of surface effects hold as well when the medium gets denser or the spheres bigger. As a further simplification of our discussion we have assumed that the distance between the atom and the granular medium is large as compared to the wavelength, so that only the leading term in a long-range expansion of the decay rate had to be retained. For smaller distances the analysis of the surface effects gets more complicated.

Appendix A. Surface effects in second order of the susceptibility

The surface contribution to the average Green function in second order of the susceptibility has been written in (5.8). It contains a product of three vacuum Green functions, the second of which is given by its short-range approximation (5.10). The contribution from the delta function in this Green function has been determined in the main text. In this appendix we shall show how the contribution from the dyadic part in (5.10) can be evaluated.

Substitution of the dyadic part of (5.10) in (5.8) with (5.9) yields the following expression:

$$\frac{z^2}{4\pi c^2}\, n\,[\chi(z)]^2\,\mathcal{P}\int^S dS''\int dh''\int^S dS'''\int dh'''\,\mathbf{G}_0(\mathbf{r},\mathbf{r}''_s+h''\,\mathbf{n}'',z)\cdot$$
$$\cdot\left\{\mathbf{I}-\frac{3}{|\mathbf{r}''_s-\mathbf{r}'''_s|^2+(h''-h''')^2}\,\left[(\mathbf{r}''_s-\mathbf{r}'''_s)\,(\mathbf{r}''_s-\mathbf{r}'''_s)+(h''-h''')^2\,\mathbf{n}''\,\mathbf{n}''\right.\right.$$
$$\left.\left.+(h''-h''')\,(\mathbf{r}''_s-\mathbf{r}'''_s)\,\mathbf{n}''+(h''-h''')\,\mathbf{n}''\,(\mathbf{r}''_s-\mathbf{r}'''_s)\right]\right\}\cdot$$
$$\cdot\mathbf{G}_0(\mathbf{r}'''_s+h'''\,\mathbf{n}'',\mathbf{r}',z)\,\bar{F}(\mathbf{r}''_s,\mathbf{r}'''_s,h'',h''')\,. \qquad \text{(A.1)}$$

The surface elements dS'' and dS''' are located at $\mathbf{r}''_s$ and $\mathbf{r}'''_s$, respectively. The normal unit vectors at these two positions are almost equal and have been denoted by $\mathbf{n}''$. The principal value sign indicates the exclusion of a small sphere around $\mathbf{r}''_s+h''\,\mathbf{n}''$ in the integrations over $\mathbf{r}'''_s$ and h'''. Furthermore, $\bar{F}(\mathbf{r}_s,\mathbf{r}'_s,h,h')$ stands for $F(\mathbf{r}_s,\mathbf{r}'_s,h,h')/[|\mathbf{r}_s-\mathbf{r}'_s|^2+(h-h')^2]^{3/2}$, while the variable z equals $\omega+\mathrm{i}0$, as before.

As in (5.4), the two Green functions in (A.1) can be expanded (in their second or first argument, respectively) around their values at $\mathbf{r}''_s$, if both $|\mathbf{r}-\mathbf{r}''_s|$ and $|\mathbf{r}'-\mathbf{r}''_s|$ are large compared to the wavelength, as we have assumed before. Up to first order in $\omega a/c$, the ensuing phase factor can be expanded as

$$1-\mathrm{i}\,\frac{z}{c}\,h''\,\mathbf{n}''\cdot\mathbf{e}_s-\mathrm{i}\,\frac{z}{c}\,h'''\,\mathbf{n}''\cdot\mathbf{e}'_s+\mathrm{i}\,\frac{z}{c}\,(\mathbf{r}''_s-\mathbf{r}'''_s)\cdot\mathbf{e}'_s \qquad \text{(A.2)}$$

since h'', h''' and $|\mathbf{r}''_s-\mathbf{r}'''_s|$ are all of order a at most. As before, $\mathbf{e}_s$ and $\mathbf{e}'_s$ are unit vectors in the direction of $\mathbf{r}-\mathbf{r}''_s$ and $\mathbf{r}'-\mathbf{r}''_s$, respectively. The product of (A.2) and the expression between curly brackets in (A.1) contains all information on the dependence of the integrand on $\mathbf{r}''_s-\mathbf{r}'''_s$. This product may be replaced by the effectively equivalent form

$$\left\{\left[-\tfrac{1}{2}\,|\mathbf{r}''_s-\mathbf{r}'''_s|^2+(h''-h''')^2\right]\,\left(1-\mathrm{i}\,\frac{z}{c}\,h''\,\mathbf{n}''\cdot\mathbf{e}_s-\mathrm{i}\,\frac{z}{c}\,h'''\,\mathbf{n}''\cdot\mathbf{e}'_s\right)\,(\mathbf{I}-3\,\mathbf{n}''\mathbf{n}'')\right.$$
$$\left.-\tfrac{3}{2}\,\mathrm{i}\,\frac{z}{c}\,(h''-h''')\,|\mathbf{r}''_s-\mathbf{r}'''_s|^2\,\left(\mathbf{e}'_s\,\mathbf{n}''+\mathbf{n}''\,\mathbf{e}'_s-2\,\mathbf{n}''\mathbf{n}''\,\mathbf{n}''\cdot\mathbf{e}'_s\right)\right\}$$
$$\times[|\mathbf{r}''_s-\mathbf{r}'''_s|^2+(h''-h''')^2]^{-1} \qquad \text{(A.3)}$$

up to first order in $\omega a/c$, when use is made of the rotation symmetry of the integration over $\mathbf{r}'''_s$ in the planar surface through $\mathbf{r}''_s$ and orthogonal to $\mathbf{n}''$. This symmetry implies that the product $(\mathbf{r}''_s-\mathbf{r}'''_s)\,(\mathbf{r}''_s-\mathbf{r}'''_s)$ may be replaced by $\frac{1}{2}\,|\mathbf{r}''_s-\mathbf{r}'''_s|^2\,(\mathbf{I}-\mathbf{n}''\mathbf{n}'')$.

To simplify the multiple integral in (A.1) we introduce, instead of h'' and h''', their sum and difference as new integration variables. Subsequently, we carry out the integral over $h''+h'''$, at fixed $h''-h'''$. Inspecting the result, one finds that in leading order of $\omega a/c$ the expression (A.1) vanishes owing to the odd parity of the integrand in its variable $h''-h'''$. The contribution from the next order in $\omega a/c$ does not vanish. It can be determined by first considering the integrations that are hidden

in the definition of the function F, as given in (5.9). These lead to the following integrals:

$$I_1(\mathbf{r}_s, h) = \int^S dS' \int dh'\, \theta[a^2 - |\tfrac{1}{2}\,\mathbf{r}_s - \mathbf{r}'_s|^2 - (\tfrac{1}{2}\,h - h')^2] \\ \times\theta[a^2 - |\tfrac{1}{2}\,\mathbf{r}_s + \mathbf{r}'_s|^2 - (\tfrac{1}{2}\,h + h')^2] \qquad \text{(A.4)}$$

$$I_2(\mathbf{r}_s, h) = \int^S dS' \int dh'\, h'^2\, \theta[a^2 - |\tfrac{1}{2}\,\mathbf{r}_s - \mathbf{r}'_s|^2 - (\tfrac{1}{2}\,h - h')^2] \\ \times\theta[a^2 - |\tfrac{1}{2}\,\mathbf{r}_s + \mathbf{r}'_s|^2 - (\tfrac{1}{2}\,h + h')^2] \qquad \text{(A.5)}$$

with $h > 0$. In writing these integrals we have chosen the origin of the coordinate system to be situated at the surface. Both of the integrals vanish for $r \equiv [|\mathbf{r}_s|^2 + h^2]^{1/2} \geq 2\,a$.

In terms of the above integrals the contribution (A.1) to the average Green function becomes in leading order of $\omega a/c$:

$$-\,\mathrm{i}\frac{z^3}{4\pi c^3}\, n\,[\chi(z)]^2\, \mathcal{P} \int^S dS'' \int^S dS''' \int dh'''\, [|\mathbf{r}''_s - \mathbf{r}'''_s|^2 + (h'' - h''')^2]^{-5/2}\, \mathsf{G}_0(\mathbf{r}, \mathbf{r}''_s, z) \cdot \\ \cdot \big[[-\tfrac{1}{2}\,|\mathbf{r}''_s - \mathbf{r}'''_s|^2 + (h'' - h''')^2]\, \big\{[\tfrac{1}{2} I_2 - \tfrac{1}{8}(h'' - h''')^2\, I_1]\, \mathbf{n}'' \cdot (\mathbf{e}_s + \mathbf{e}'_s) \\ + \tfrac{1}{4}(h'' - h''')^2\, I_1\, \mathbf{n}'' \cdot (\mathbf{e}_s - \mathbf{e}'_s)\big\}\, (\mathsf{I} - 3\,\mathbf{n}''\mathbf{n}'') \\ + \tfrac{3}{4}\,(h'' - h''')^2\, |\mathbf{r}''_s - \mathbf{r}'''_s|^2\, I_1\, (\mathbf{e}'_s\, \mathbf{n}'' + \mathbf{n}''\, \mathbf{e}'_s - 2\,\mathbf{n}''\, \mathbf{n}''\, \mathbf{n}'' \cdot \mathbf{e}'_s)\big] \cdot \mathsf{G}_0(\mathbf{r}''_s, \mathbf{r}', z) \qquad \text{(A.6)}$$

with I_1 and I_2 depending on $\mathbf{r}''_s - \mathbf{r}'''_s$ and $h'' - h'''$.

In order to proceed we have to determine explicit expressions for the integrals I_1 and I_2. The first is the standard overlap integral, which has been encountered in (4.4). It equals $v_0\, c(r)$, with $c(r)$ given in (4.7). The integral I_2 is the second moment of the overlap integral. Choosing cartesian coordinates in such a way that the normal to the surface at the origin points in the direction of the positive z-axis, and that $\mathbf{r}_s$ equals $(x, 0, 0)$ with $x > 0$, we may write (A.5) as

$$I_2(\mathbf{r}_s, h) = \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dh'\, h'^2\, \theta\left[a^2 - (\tfrac{1}{2}x - x')^2 - y'^2 - (\tfrac{1}{2}h - h')^2\right] \\ \times\theta\left[a^2 - (\tfrac{1}{2}x + x')^2 - y'^2 - (\tfrac{1}{2}h + h')^2\right]\, . \qquad \text{(A.7)}$$

The integral over y' is trivial, with the result

$$I_2(\mathbf{r}_s, h) = 4 \int_{-\infty}^{\infty} dh'\, h'^2 \int_{-hh'/x}^{\infty} dx'\, \left[a^2 - (\tfrac{1}{2}x + x')^2 - (\tfrac{1}{2}h + h')^2\right]^{1/2} \\ \times\theta\left[a^2 - (\tfrac{1}{2}x + x')^2 - (\tfrac{1}{2}h + h')^2\right]\, . \qquad \text{(A.8)}$$

The θ-function constrains the integrations over x' and h'. This constraint interferes with the bounds on the integration written explicitly in (A.8). By a geometrical analysis one finds that the interference depends on the sign of the combination $x^2 + h^2 - 2\,a\,h$. In fact, for $2\,a\,h \leq x^2 + h^2 \leq 4\,a^2$ the upper limit of the x'-integration is effectively finite, while the lower limit is left unchanged. Furthermore, the domain of the h'-integral is found to be constrained to values $|h'| \leq M$, with $M = x\,[(a^2 - \frac{1}{4}\,x^2 - \frac{1}{4}\,h^2)/(x^2 + h^2)]^{1/2}$. Hence, after a shift of the x'-variable one has the following for $2\,a\,h \leq x^2 + h^2 \leq 4\,a^2$:

$$I_2(\mathbf{r}_s, h) = 4 \int_{-M}^{M} dh'\, h'^2 \int_{-hh'/x + x/2}^{[a^2 - (h/2 + h')^2]^{1/2}} dx'\, \left[a^2 - x'^2 - (\tfrac{1}{2}h + h')^2\right]^{1/2}\, . \qquad \text{(A.9)}$$

The integral over x' yields the result

$$\tfrac{1}{4}\,\pi\,\left[a^2-(\tfrac{1}{2}\,h+h')^2\right]-\tfrac{1}{2}\left(\tfrac{1}{2}\,x-\frac{h\,h'}{x}\right)\,\left[a^2-\tfrac{1}{4}\,x^2-\tfrac{1}{4}\,h^2-h'^2\,\frac{x^2+h^2}{x^2}\right]^{1/2}$$
$$-\tfrac{1}{2}\,\left[a^2-(\tfrac{1}{2}\,h+h')^2\right]\,\arcsin\left[\left(\tfrac{1}{2}\,x-\frac{h\,h'}{x}\right)\Big/\left[a^2-(\tfrac{1}{2}\,h+h')^2\right]^{1/2}\right]\,. \qquad (A.10)$$

After a partial integration in order to get rid of the arcsine function, the integral over h' can be carried out as well. The final result is

$$I_2(\mathbf{r}_s,h)=\frac{\pi}{\sqrt{x^2+h^2}}\,\left[a^4\,\left(-\tfrac{1}{4}\,x^2-\tfrac{1}{2}\,h^2\right)+a^2\,\left(\tfrac{1}{24}\,x^4-\tfrac{1}{24}\,x^2\,h^2-\tfrac{1}{12}\,h^4\right)\right.$$
$$\left.-\tfrac{1}{320}\,x^6-\tfrac{1}{240}\,x^4\,h^2+\tfrac{1}{960}\,x^2\,h^4+\tfrac{1}{480}\,h^6\right]+\tfrac{1}{15}\,\pi\,a^3\,\left(4\,a^2+5\,h^2\right) \qquad (A.11)$$

for $2\,a\,h\leq x^2+h^2\leq 4\,a^2$.

In the other case $x^2+h^2<2\,a\,h$ the double integral is the sum of two contributions with different bounds:

$$I_2(\mathbf{r}_s,h)=4\int_{-M}^{M}dh'\,h'^2\int_{-hh'/x+x/2}^{[a^2-(h/2+h')^2]^{1/2}}dx'\,\left[a^2-x'^2-(\tfrac{1}{2}h+h')^2\right]^{1/2}$$
$$+4\int_{M}^{-h/2+a}dh'\,h'^2\int_{-[a^2-(h/2+h')^2]^{1/2}}^{[a^2-(h/2+h')^2]^{1/2}}dx'\,\left[a^2-x'^2-(\tfrac{1}{2}h+h')^2\right]^{1/2}\,. \qquad (A.12)$$

Upon evaluating the x'- and the h'-integral we arrive at a result that is found to be identical to that given in (A.11).

Employing spherical coordinates in (A.11), with $h=r\,\cos\theta$ and $x=r\,\sin\theta$, we may write the second moment of the overlap integral for both cases as

$$I_2(\mathbf{r}_s,h)=v_0\,a^2\,\left[\frac{1}{5}-\frac{3r}{16a}\,(1+\cos^2\theta)+\frac{r^2}{4a^2}\,\cos^2\theta+\frac{r^3}{32a^3}\,(1-3\,\cos^2\theta)\right.$$
$$\left.-\frac{r^5}{1280a^5}\,(3-5\,\cos^2\theta)\right]\,\theta(2\,a-r)\,. \qquad (A.13)$$

Having obtained explicit expressions for I_1 and I_2, we return to (A.6). The integrals over $\mathbf{r}_s'''$ (with surface element dS''') and h''' can be calculated straightforwardly upon introducing spherical coordinates and performing the angular integration first. In this way we arrive at the result

$$-\,\mathrm{i}\,\frac{z^2}{25c^2}\,n\,v_0\,[\chi(z)]^2\,a\,q\int^{S}dS''\,\mathbf{G}_0(\mathbf{r},\mathbf{r}_s'',z)\cdot(-\tfrac{2}{3}\,\mathbf{I}\,\mathbf{n}''\cdot\mathbf{e}_s'+\mathbf{e}_s'\,\mathbf{n}''+\mathbf{n}''\,\mathbf{e}_s')\,\cdot$$
$$\cdot\mathbf{G}_0(\mathbf{r}_s'',\mathbf{r}',z)\,. \qquad (A.14)$$

This is equivalent to (5.12), since one may use the identity $\mathbf{e}_s'\cdot\mathbf{G}(\mathbf{r}_s'',\mathbf{r}',z)=0$ for distances $|\mathbf{r}'-\mathbf{r}_s''|$ that are large compared to the wavelength.

Appendix B. Scattering fields in Mie theory

Electromagnetic scattering from a dielectric sphere has first been treated by Mie [30] and reviewed subsequently by several authors [31, 32]. If a linearly polarized incoming plane wave, with the wave vector $\mathbf{k}$ in the direction of the positive z-axis, with the polarization vector $\mathbf{e}_\sigma$ along the x-axis and with the amplitude E_0, impinges on a dielectric sphere with a radius a, with centre at the origin and with a dielectric constant

$\varepsilon = 1 + \chi$, the components of the scattered electric field in the far-field region have the form [32]

$$E_\theta^{(s)}(r,\theta,\varphi) = E_0 \,\frac{\mathrm{e}^{\mathrm{i}kr}}{kr}\, \cos\varphi \sum_{\ell=1}^{\infty} (-\mathrm{i})^\ell \, [B_\ell^e \, \tau_\ell(\cos\theta) + B_\ell^m \, \pi_\ell(\cos\theta)]$$
$$E_\varphi^{(s)}(r,\theta,\varphi) = -E_0 \,\frac{\mathrm{e}^{\mathrm{i}kr}}{kr}\, \sin\varphi \sum_{\ell=1}^{\infty} (-\mathrm{i})^\ell \, [B_\ell^e \, \pi_\ell(\cos\theta) + B_\ell^m \, \tau_\ell(\cos\theta)] \tag{B.1}$$

with spherical coordinates r, θ and φ. The angular functions are defined in terms of associated Legendre polynomials as

$$\pi_\ell(\cos\theta) = \frac{1}{\sin\theta}\, P_\ell^1(\cos\theta) \quad , \quad \tau_\ell(\cos\theta) = \frac{d}{d\theta}\, P_\ell^1(\cos\theta)\,. \tag{B.2}$$

The electric and magnetic multipole amplitudes read

$$B_\ell^p = \mathrm{i}^{\ell+1}\, \frac{2\ell+1}{\ell(\ell+1)}\, \frac{N_\ell^p}{D_\ell^p} \tag{B.3}$$

with $p = e, m$. The numerators and denominators are given as

$$N_\ell^e = \varepsilon\, [(\ell+1)\, j_\ell(q) - q\, j_{\ell+1}(q)]\; j_\ell(q') - [(\ell+1)\, j_\ell(q') - q'\, j_{\ell+1}(q')]\; j_\ell(q)$$
$$N_\ell^m = [(\ell+1)\, j_\ell(q) - q\, j_{\ell+1}(q)]\; j_\ell(q') - [(\ell+1)\, j_\ell(q') - q'\, j_{\ell+1}(q')]\; j_\ell(q)$$
$$D_\ell^e = \varepsilon\, \Big[(\ell+1)\, h_\ell^{(1)}(q) - q\, h_{\ell+1}^{(1)}(q)\Big]\; j_\ell(q') - [(\ell+1)\, j_\ell(q') - q'\, j_{\ell+1}(q')]\; h_\ell^{(1)}(q)$$
$$D_\ell^m = \Big[(\ell+1)\, h_\ell^{(1)}(q) - q\, h_{\ell+1}^{(1)}(q)\Big]\; j_\ell(q') - [(\ell+1)\, j_\ell(q') - q'\, j_{\ell+1}(q')]\; h_\ell^{(1)}(q) \tag{B.4}$$

with spherical Bessel and Hankel functions depending on $q = ka$ and $q' = \sqrt{\varepsilon}\, q$.

For small values of q, the first few multipole amplitudes get the form

$$B_1^e = \mathrm{i}\, q^3\, \frac{\chi}{3+\chi}\left(1 - \frac{3}{5}\, q^2\, \frac{1-\chi}{3+\chi} + \frac{2\mathrm{i}}{3}\, q^3\, \frac{\chi}{3+\chi}\right)$$
$$B_2^e = -\frac{1}{18}\, q^5\, \frac{\chi}{5+2\chi}$$
$$B_1^m = \frac{\mathrm{i}}{30}\, q^5\, \chi \tag{B.5}$$

up to the order q^6. When χ is small as well, the first two of these can be written as

$$B_1^e = \frac{\mathrm{i}}{3}\, q^3\, \chi\, \left[1 - \frac{1}{3}\,\chi - \frac{1}{5}\, q^2\, \left(1 - \frac{5}{3}\,\chi\right) + \frac{2\mathrm{i}}{9}\, q^3\, \chi\right]$$
$$B_2^e = -\frac{1}{90}\, q^5\, \chi \left(1 - \frac{2}{5}\,\chi\right) \tag{B.6}$$

up to the order χ^2. Upon substitution in (B.1) the far fields are found as

$$E_\theta^{(s)}(r,\theta,\varphi) = E_0\, \frac{\mathrm{e}^{\mathrm{i}kr}}{kr}\, q^3\, \chi\, \cos\varphi\, \left\{\frac{1}{3}\, \left(1 - \frac{1}{5}\, q^2\right) \cos\theta + \frac{1}{15}\, q^2\, \cos^2\theta\right.$$
$$\left. +\chi\, \left[-\frac{1}{9}\left(1 - q^2 - \frac{2\mathrm{i}}{3}\, q^3\right) \cos\theta - \frac{1}{75}\, q^2\, \left(2\,\cos^2\theta - 1\right)\right]\right\}$$
$$E_\varphi^{(s)}(r,\theta,\varphi) = -E_0\, \frac{\mathrm{e}^{\mathrm{i}kr}}{kr}\, q^3\, \chi\, \sin\varphi\, \left\{\frac{1}{3}\, \left(1 - \frac{1}{5}\, q^2\right) + \frac{1}{15}\, q^2\, \cos\theta\right.$$
$$\left. +\chi\, \left[-\frac{1}{9}\left(1 - q^2 - \frac{2\mathrm{i}}{3}\, q^3\right) - \frac{1}{75}\, q^2\, \cos\theta\right]\right\} \tag{B.7}$$

up to the order q^6 and χ^2. In vectorial notation this expression may be rewritten by introducing the long-range form of the vacuum Green function (4.11):

$$\mathbf{E}^{(s)}(\mathbf{r}) = -\frac{\omega^2}{c^2}\, v_0\, \chi\, \mathsf{G}_0(\mathbf{r}, 0, \omega + \mathrm{i}0) \cdot \left\{ \mathsf{I} \left(1 - \frac{1}{5}\, q^2 + \frac{1}{5}\, q^2\, \hat{\mathbf{r}} \cdot \hat{\mathbf{k}} \right) \right.$$
$$\left. + \chi \left[\mathsf{I} \left(-\frac{1}{3} + \frac{1}{3}\, q^2 + \frac{2\mathrm{i}}{9}\, q^3 \right) - \frac{1}{25} q^2 \left(\mathsf{I}\, \hat{\mathbf{r}} \cdot \hat{\mathbf{k}} + \hat{\mathbf{k}}\, \hat{\mathbf{r}} \right) \right] \right\} \cdot \mathbf{E}_i(0) \tag{B.8}$$

with the spherical volume $v_0 = 4\,\pi\, a^3/3$ and with the unit vectors $\hat{\mathbf{r}} = \mathbf{r}/r$ and $\hat{\mathbf{k}} = \mathbf{k}/k$. This expression for the scattered electric field is consistent with that found in (5.17) for the average field due to scattering from a set of Mie spheres.

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